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Preparation of large single grains of the quasicrystalline icosahedral Al–Cu–Fe ψ phase

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Preparation of large single grains of the quasicrystalline icosahedral Al–Cu–Fe ψ phase

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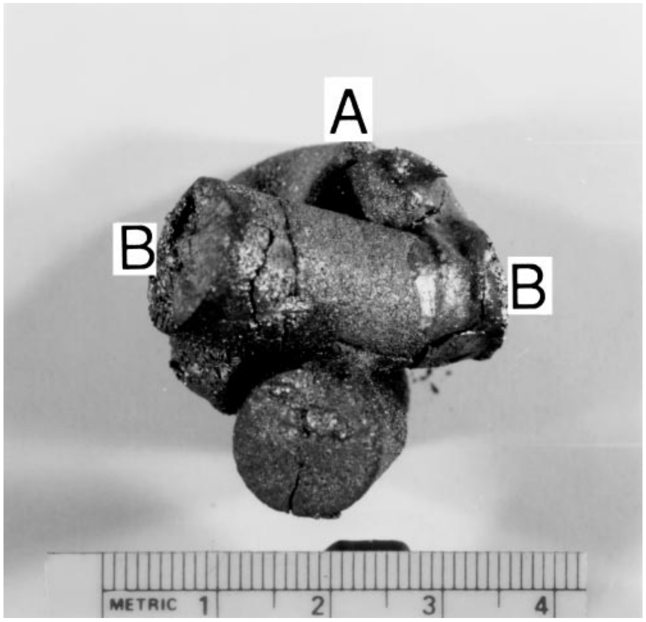
A cyclic heat-treatment process was used to prepare single grains of the quasicrystalline icosahedral phase, ψ–$Al_{65}Cu_{23}Fe_{12}$. Alloys of appropriate composition are melted and chill cast into copper molds. Multiple cyclic heat treatments at successively higher temperatures below 860 °C, the peritectic decomposition temperature of the quasicrystal phase, are used to enhance the growth of the ψ phase. Single grains up to 10 mm $\times$ 5 mm $\times$ 5 mm have been prepared.

The phase equilibria of most alloy systems[1–6] which contain a quasicrystalline phase is such that conventional crystal growth techniques, for example, Bridgman, Czochralski, etc., are not successful in preparing large crystals of the quasicrystalline phase. The ψ phase of the Al–Cu–Fe alloy system is no exception, forming during solidification through a peritectic involving liquid and two crystalline solids.[23] As a result, the face-centered icosahedral (FCI) ψ phase does not form directly from the liquid, but is the product of a peritectic solidification reaction at ≈860 °C between two high-temperature crystalline phases and liquid; $L + \beta(\mathrm{FeCuAl}) + \lambda(\mathrm{Al_{13}Fe_4}) \rightarrow \psi(\mathrm{FCI})$. Previous work on preparing single crystals in this system.[7–9] used an annealing method in which multiphase samples were heated to just below the peritectic reaction at 860 °C. Therefore, most single grain quasicrystalline samples have been extracted from bulk ingots with gain sizes typically less than a millimeter in size. Ishimasa and Mori,[10] using a slow cooling process through the peritectic reaction followed by a short anneal at 822 °C, were able to produce single grains of the Al–Cu–Fe ψ phase of up to 3 m. In this communication, we describe a process whereby multiple isothermal heat treatments at temperatures below the peritectic reaction have been used to enhance the growth of the ψ phase, resulting in single grains up to 10 mm $\times$ 5 mm $\times$ 5 mm in size.

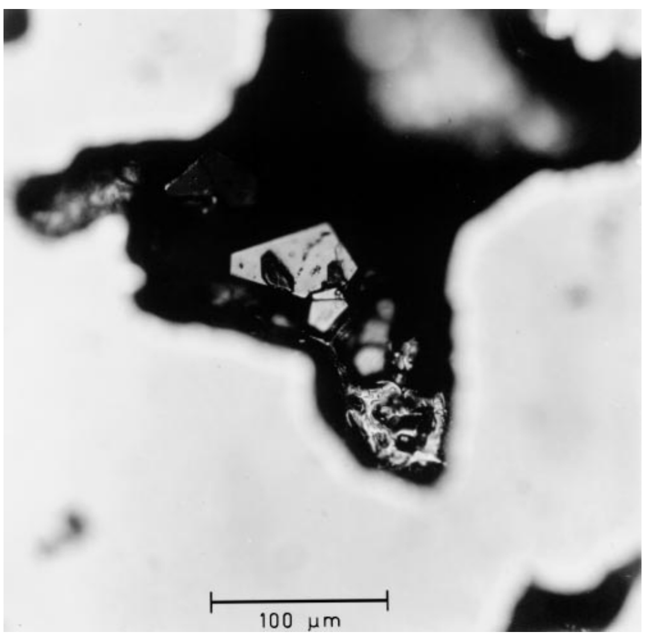
Appropriate quantities of aluminum, copper, and iron (99.99% purity, metals basis) are cleaned and arc melted into buttons weighing approximately 50 g. The buttons are melted up to four times under an argon atmosphere to ensure compositional homogeneity in the buttons. The buttons are then drop cast into a copper chill mold into ingots roughly 1/2 inch in diameter and 2–3 inches long. Three different heat treatments were used to prepare single grains of the ψ phase: (i) continuous isothermal anneal at 800 °C for 14 days; (ii) isothermal anneal at 800 °C for three days, furnace cool to 25 °C, and isothermal anneal at 800 °C for an additional 11 days; and (iii) isothermal anneal at 800 °C for 3 days then furnace cool to 25 °C, isothermal anneal at 810 °C for 10 days and furnace cool to 25 °C, and isothermal anneal at 825 °C for 7 days.

Of the three different heat treatments applied to the chill cast ingots, only the latter two resulted in significant growth of the icosahedral ψ phases. The development of the single grains of the ψ phase could be traced after each intermediate furnace cool. Following furnace cooling from 800 °C after three days, the ingot had broken into several pieces and the surface of the ingot change from a smooth as-cast appearance to a porous surface, as shown in region A of Fig. 1(a). Within the porous regions of the ingot, small crystallites with pentagonal facets could be observed, as shown in Fig. 1(b). Following further heat treatment at 810 °C and then 825 °C, large grains appeared at both ends of the ingot in a manner similar to that reported by Ishimasa and Mori,[10] as indicated in Fig. 1(a) (region B). Also noticeable was the large amount of liquid generated at these temperatures which accumulated at the bottom of the crucible during these anneals. The single grains were extracted from the ingots mechanically, and one of the largest is shown in Fig. 2(a). The surface of these crystals did exhibit some facets which were identified using back reflection Laue diffraction, Fig. 2(b), as planes of fivefold symmetry. A powder x-ray diffraction pattern, shown in Fig. 3, taken of a crushed single grain was used to verify the icosahedral crystal structure.

Chemical analysis by inductively coupled plasma-atomic emission spectroscopy of both the single grains and the porous regions of the ingot is given in Table I. Comparison of the measured composition of the single grains with isothermal sections of the Al–Cu–Fe phase diagrams[2,3] indicates that the composition of the single grains lies within the two-phase region, $\psi + \lambda$. Metallographic examination and scanning electron microscopy

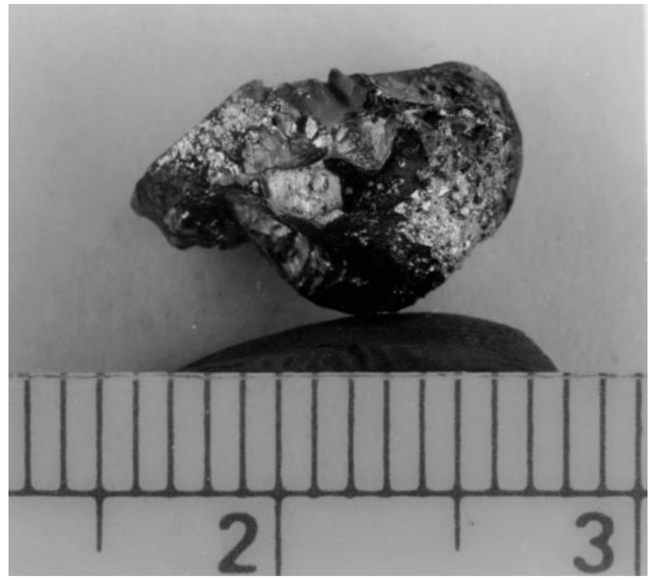


(a)

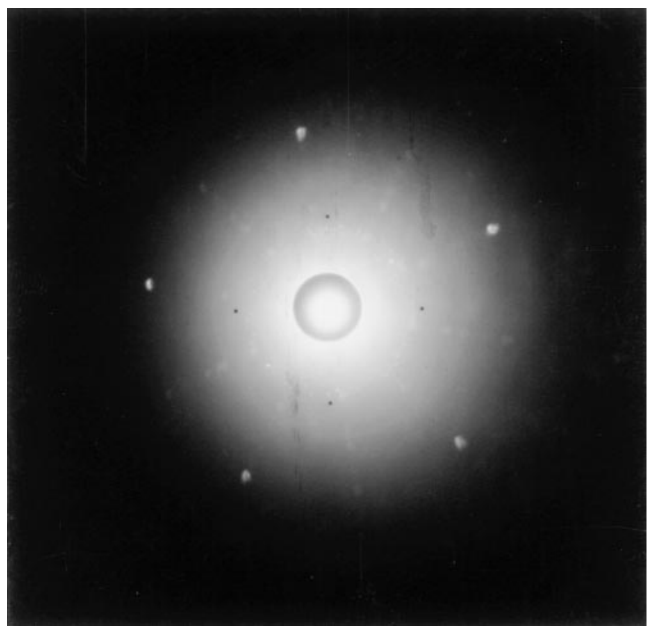


(b)

FIG. 1. (a) Photograph of the as-annealed ingot. The original ingot has broken into three pieces and the majority of the surface has developed a porous nature (region A). The single grains have formed at the ends of these pieces (region B). (b) Photomicrograph of the small faceted grains found within the porous region.



(a)



(b)

FIG. 2. (a) Photograph of one of the largest grains extracted from the ingot. (b) Back reflection Laue photograph of the facets on the crystal, indicating the facets possess fivefold symmetry.

verified λ particles are present within a matrix of ψ. Further examination of the single grain also revealed other two-phase areas scattered across the surface, which were identified as containing the ω (Al_7Cu_2Fe) and θ (Al_2Cu) phases, consistent with the decomposition Ishiasa and Mori reported during slow cooling of the ψ phase. The matrix of the single grain was restored to single phase ψ by reheating at 800 °C and quenching.

The growth of large grains of the ψ phase at isolated spots along the ingot is somewhat remarkable in two ways. Isothermal annealing of metal alloys usually results in a uniform increase in grain size. Generally this behavior is unaffected by a temperature cycling with the exception of abnormal grain growth[11,12] which occurs during the latter stages of grain growth and can be initiated by increases in the annealing temperature.

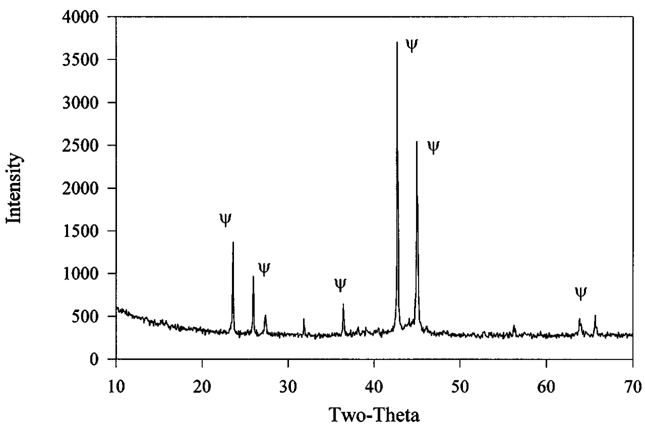


FIG. 3. Powder diffraction pattern of a crushed single grain of the ψ phase. All peaks index to the face-centered icosahedral structure.

TABLE I. Chemical compositions of the various regions of the ingot by ICP-AES.

Region	Chemical composition
Nominal	$Al_{65}Cu_{23}Fe_{12}$
Porous	$Al_{64.5}Cu_{25}Fe_{10.5}$
Single grain	$Al_{64.5}Cu_{22}Fe_{13.5}$

However, abnormal grain growth is normally observed in single phase material and is usually inhibited by second phases which act as pinning sites for grain boundary motion. Second, isothermal annealing would tend to reduce any chemical inhomogeneities within the ingot. However, the compositional analysis of the porous regions versus the single grains shows a large chemical difference between these portions of the ingot. What could give rise to this chemical segregation and how this may influence the growth of single grains of the ψ phase remains under investigation.

In summary, large single grains of the icosahedral ψ phase of the Al–Cu–Fe system have been prepared using a cyclic heat-treatment process. The grains exhibit some faceting associated with planes of fivefold symmetry. Chemical analysis indicates large compositional shifts from the nominal composition, resulting in the grains of ψ being two phase. The exact nature of the chemical segregation and its influence on the formation of the ψ phase is under investigation.

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